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Synthetic phenolic antioxidants and transformation products in dust from different indoor environments in Toronto, Canada

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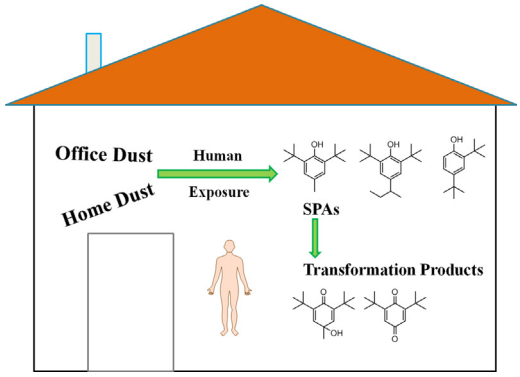
HIGHLIGHTS

- Eight SPAs were detected for the first time in indoor dust from Canada.
- Four transformation products of BHT were also identified.
- Similar target concentrations were found for office and home dust.
- Indoor dust ingestion is a minor human exposure pathway for BHT.

GRAPHICAL ABSTRACT



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ABSTRACT

Synthetic phenolic antioxidants (SPAs) are a class of anthropogenic antioxidants that are widely used in a large variety of commercial products. Although several SPAs have been listed as targets for risk assessment by Environment and Climate Change Canada, little data are available on the occurrence of SPAs in the Canadian environment. In this study, eighty-three indoor dust samples were collected from offices and homes in Toronto. Eight SPAs were detected at concentrations ranging from 67.2 to 1.55e4 ng/g, with a geometric mean (GM) concentration of 1.49e3 ng/g, among which 2,6-di-*tert*-butyl-4-methylphenol (BHT) was the primary congener and had a GM concentration of 658 ng/g. Four BHT transformation products (TPs) were also detected in the indoor dust samples, with concentrations ranging from 40.4 to 1.27e4 ng/g and a GM concentration of 883 ng/g. No significant concentration difference was observed between the office and home dust samples for either the summed target SPA or TP concentrations ($p > 0.05$). The calculated estimated daily intakes of these chemical contaminants (0.004–10.0 ng/kg BW/day) suggest that they pose no immediate health risk to the Canadian population. To the best of our knowledge, this is the first report of the occurrence of these chemical contaminants and their transformation products in Canadian indoor environments, and furthermore the first detection of 4-*tert*-butyl-phenol in an environmental sample.

1. Introduction

Synthetic phenolic antioxidants (SPAs) are a class of manmade antioxidants most frequently employed to retard oxidation reactions in a

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large variety of industrial and household materials including lubricants, fuels, plastics, elastomers, and synthetic fibers (Lanigan and Yamarik, 2002; Rodil et al., 2010; Rodil et al., 2012; Brocca et al., 2002). Previous studies have shown that commercial products containing SPAs can act as sources of these emerging chemical pollutants, leading to contamination of the surrounding environment (Brocca et al., 2002). For example, it has been established that SPAs migrate from plastics to water (Brocca et al., 2002). Indeed, the intensive production and massive application of SPAs over the past several decades have led to public concern about environmental contamination by these compounds. Of all SPAs that have been investigated, 2,6-di-*tert*-butyl-4-methylphenol (BHT) has received the most attention, due to its high application volume and reported toxicity effects. As the most commonly used antioxidant, BHT had a global annual production capacity of approximately 62,000 tonnes in the year 2000 (OECD, 2002). BHT has been identified in a variety of environmental matrices such as river water (Fries and Puttmann, 2004), sediment (Wang et al., 2018; Zhang et al., 2018), soil (Hernandez et al., 2012), sludge (Liu et al., 2015b; Lu et al., 2019), and indoor dust samples (Liu et al., 2017). It was even found in human serum from United States donors, at concentrations up to 22.6 ng/mL (median: 3.37 ng/mL) (Liu and Mabury, 2018b). In addition to BHT, some other SPAs, such as 2,4-di-*tert*-butylphenol (DBP), 2,4,6-tri-*tert*-butylphenol (AO246), and 2,6-di-*tert*-butyl-4-*sec*-butylphenol (DTBSBP), were also detected in sludge and dust samples collected in China, albeit at relatively low concentrations compared to BHT (Liu et al., 2017; Liu et al., 2015b).

Toxicity studies indicate that exposure to SPAs has the potential to cause health issues. Specifically, in vitro and in vivo experiments have demonstrated DBP, 4-*tert*-octylphenol (4-*t*OP), and 3-*tert*-butyl-4-hydroxyanisole (BHA) to be endocrine disruptors (Creusot et al., 2013; Jobling et al., 1995; Olsen et al., 2002; Kotula-Balak et al., 2013; Pederson et al., 1999; Yang et al., 2018a; Yang et al., 2018b). BHA was also found to be a cancerogen in rodents (Grice, 1988). Some transformation products (TPs) of BHT, such as 2,6-di-*tert*-butyl-p-benzoquinone (BHT-Q) and 3,5-di-t-butyl-4-hydroxybenzaldehyde (BHT-CHO), were found to cause cleavage of supercoiled DNA in in vitro experiments (Nagai et al., 1993).

Due to their reported toxicity effects and predicted persistence, some SPAs are on the candidate list of substances of very high concern for authorization (ECHA, 2018). For example, because of its pronounced persistence and its high tendency towards bioaccumulation and aquatic toxicity, AO246 sees only sparing industrial use in most countries, and is even forbidden in Japan (Government of Japan, 2010). Although some SPAs, such as DTBSBP, have been listed as targets for risk assessment by Environment Canada (2010), little data reporting the occurrence of any SPAs or TPs in Canadian environments are available. Determination of the concentrations of these chemical contaminants in indoor environments is crucial to evaluating their adverse health impacts on humans, as people spend, on average, 90% of their time indoors (Klepeis et al., 2001). Indoor dust is a useful matrix for evaluating the occurrence of various low volatility chemical contaminants in indoor environments (Liu and Mabury, 2018a; Liu and Mabury, 2019; Liu et al., 2016). In order to better understand the contamination level and human exposure to SPAs and related TPs in indoor environments in Canada, indoor dust samples were collected from two types of indoor environments (offices and residential houses) in Toronto. This study documents the first assessment of the occurrence, concentrations, composition profiles, and human exposure of these emerging SPAs and related TPs in indoor environments in Canada.

2. Materials and methods

2.1. Materials

Information such as target abbreviations and structures are shown in Fig. 1, and their names and other related information are listed in Table S1. Native standards of the target SPAs and TPs were obtained from TCI Inc. (Tokyo, Japan) and Sigma-Aldrich (Oakville, Canada). An isotope-labeled standard of 2,6-di-(*tert*-butyl-d_9)-4-methyl(phenol-3,5,O-d_3) (BHT-d_{21}) was supplied by Cambridge Isotope Laboratories (Andover, MA). HPLC-grade acetonitrile (ACN), methanol (MeOH), and methyl *tert*-butyl ether (MTBE) were purchased from Sigma-Aldrich (Oakville, Canada).

2.2. Dust samples

Eighty-three dust samples were collected from different indoor environments in Toronto in 2018. Among, 29 dust samples were collected from residential houses while 54 samples were obtained from offices. Only one dust sample was collected from each house or office. Using a vacuum cleaner with a 4 × 4 inch cotton pad attached on the tube extender, the dust samples were obtained from the surfaces of furniture, windowsills and so on. A new cotton pad, which was pre-cleaned with MeOH, was employed to obtain each dust sample. Large debris, such as hair, were removed from the dust samples using tweezers. The dust samples were not further sieved. Field blank samples were prepared by collecting sodium sulfate with the same method for dust samples. All indoor dust samples and field blanks were packed in aluminum foil, put in polypropylene bags, and kept in a freezer at −20 °C awaiting further pretreatment and analysis. More details on the dust samples can be found in our previous study (Liu and Mabury, 2019).

2.3. Sample preparation and quantitative analysis

A simple pretreatment method was developed to prepare the dust samples for SPA and TP analysis. Briefly, 0.1 g of dust sample (containing 100 ng of BHT-d_{21}) was put in a glass tube and extracted with ACN (3 mL) by shaking at 400 rotations per minute (rpm) for 30 min. The sample was then centrifuged and the ACN was moved to another glass tube. The above procedures were conducted three times on each dust sample. The three ACN extracts were combined, dried under nitrogen, and then dissolved in 1 mL of MTBE. Finally, this solvent-exchanged sample was further centrifuged to remove suspended particles, and then a 1 μL aliquot was injected into the instrument for analysis of target molecules.

All the SPA and TP targets were analyzed by a gas chromatography–mass spectrometry (GC–MS) equipped with an electron ionization (EI) source. In the present study, a 7890A gas chromatograph coupled to a 5973C triple-axis mass detector (Agilent, Santa Clara, CA) was used for the target analysis. A DB-1701 column (30 m × 0.25 mm × 0.25 μm, Agilent Technologies, Palo Alto, CA) was used for the target separation. The flow of helium was set to 1.0 mL/min. The oven program was started at 80 °C, held for 5 min, increased to 200 °C at a rate of 6 °C/min, and then increased to 250 °C at a rate of 50 °C/min. Splitless injection was used, with an inlet temperature of 240 °C. The injection volume was 1 μL. Selected ion monitoring (SIM) mode was used. Detailed information on the selected ions and retention times for the targets were shown in Table S2.

2.4. Quality assurance and quality control

To examine whether three extraction cycles were sufficient to extract most SPAs and TPs from the dust samples, a fourth extraction was conducted on eight randomly selected indoor dust samples. For all SPAs and TPs, the residual concentrations in the fourth extraction were <2% of the corresponding target concentrations resulting from the previous three extractions, indicating that three extraction cycles were good enough for all target SPAs and TPs. As shown in Table S3, recoveries of the target SPAs and TPs in the spiked indoor dust samples (low spiking level: 50 ng/g, high spiking level: 500 ng/g) varied from 89 to 113% and 85 to 118%, respectively ($n = 3$). The relative standard deviations were all <15% at both spiking levels ($n = 3$). One procedural

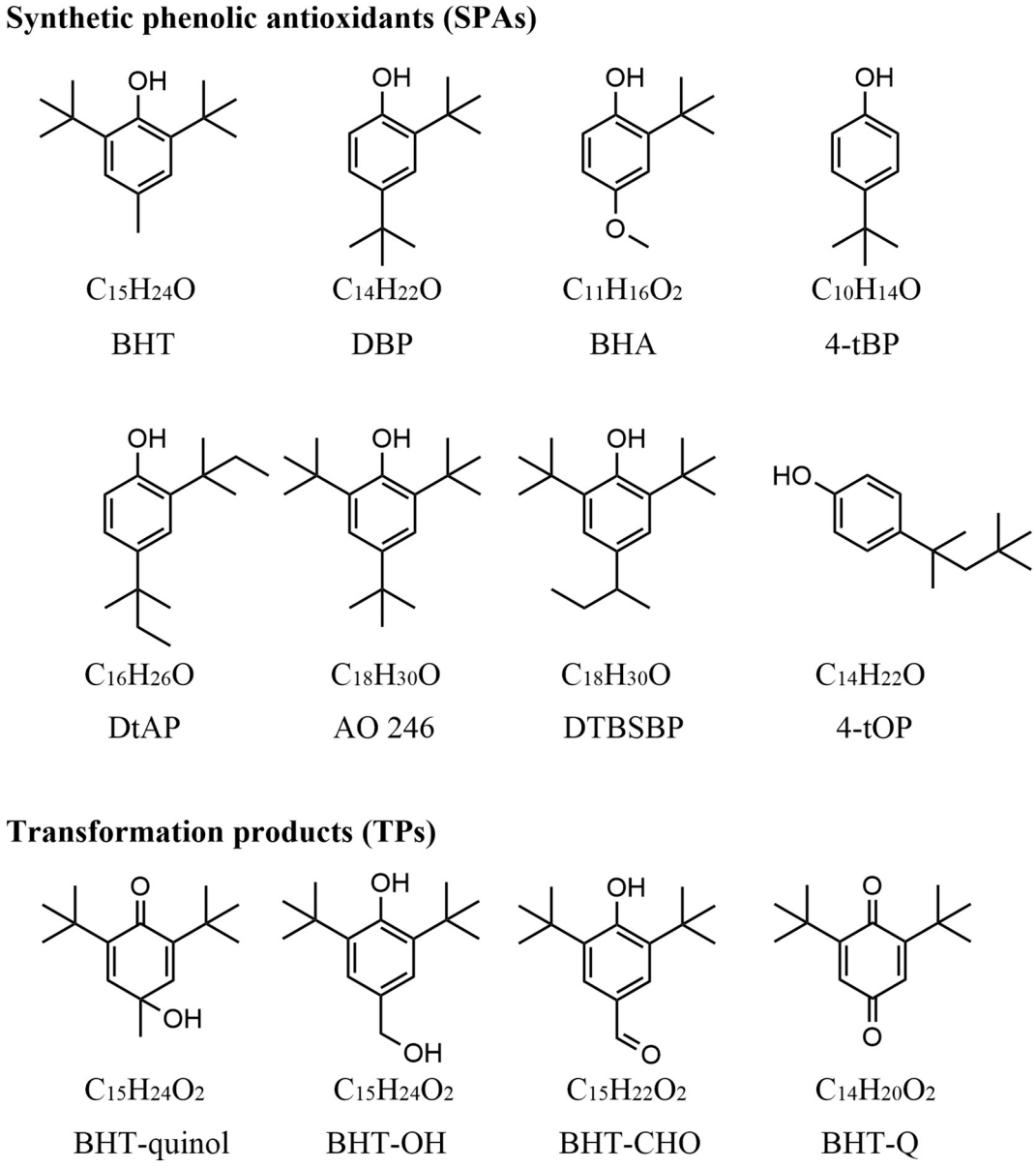

Fig. 1. Structures, molecular formulas, and abbreviations of SPAs and TPs.

blank was extracted in every batch of 10 samples. BHT and DBP were occasionally detected in the procedural blank samples but the blanks never contributed >4% to the averaged concentrations in the sample batch of dust samples. In addition, no SPAs or TPs were detected in the field blank samples, suggesting no target contamination during the sample collection. Method quantification limits (MQLs) of BHT (2 ng/g) and DBP (4 ng/g) were defined as 3 times of standard deviation of the detected concentrations in procedural blanks. MQLs of the other targets, which were not detected in procedural blanks, were calculated as a signal-to-noise ratio of 10 and ranged from 0.3 to 20 ng/g. The linear dynamic range of instrumental response was verified daily by a calibration curve with a minimum concentration set to the MQLs and a maximum concentration of 200 ng/mL. The calibration was found to be linear from 5 to 200 ng/mL for DBP. Dust samples with SPA or TP concentrations higher than the linear range were diluted with MTBE before injection. Recoveries of BHT-d_{21} in the 83 real indoor dust samples were 62–106% (mean: 88%). Target concentrations in the real indoor dust samples were corrected using the BHT-d_{21} internal standard.

2.5. Statistical analysis

Statistical analysis of the SPA and TP concentrations was carried out with SPSS version 19.0 (SPSS Inc. 2010). In this study, the geometric mean (GM), median, and concentration range were included to express the concentrations of the target SPAs and TPs in the indoor dust samples. SPA and TP concentrations lower than the MQLs were defined as the MQLs divided by the square root of 2. Spearman's test (2-tailed) was used to assess correlations among the SPA and TP residue levels in the indoor dust samples. SPAs and TPs with low quantification frequency (<50%) were excluded from the statistical analysis. Mann-Whitney *U* test was used to determine the significance of the concentration difference between office and home indoor environments. $\sum$SPAs is the sum of the concentrations of all the target SPAs detected in the indoor dust samples, while $\sum$TPs is the sum of the concentrations of all TPs detected. The composition profiles of the SPAs and TPs are defined as the percent contributions of individual analogues to the total concentrations in each indoor dust sample.

3. Results and discussion

3.1. SPAs in indoor dust

All eight target SPAs were detected in the collected indoor dust samples (Table 1), with ∑SPAs ranging from 67.2 to 1.55e4 ng/g (GM: 1.49e3 ng/g). BHT was detected in 96% of the indoor dust samples at concentrations of <MQL–1.52e4 ng/g (GM: 658 ng/g). DBP was also identified in most of the indoor dust samples (96%) with concentrations from <MQL to 2.27e3 ng/g (GM: 161 ng/g). 4*t*OP was detected in 93% of the samples, with concentrations from <MQL to 844 ng/g (GM: 127 ng/g). 4-*tert*-Butyl-phenol (4*t*BP), which has a similar structure to 4*t*OP, was only detected in 53% of the samples and at relatively low concentrations (<MQL–1.34e3 ng/g, GM: 19.7 ng/g). AO246, which has been detected at high concentrations in dust (GM: 323 ng/g, $n = 75$) and sludge (GM: 374 ng/g, $n = 56$) in China (Liu et al., 2017; Liu et al., 2015b), was only detected in 11% of the samples and at very low concentrations (<MQL–177 ng/g, GM: 0.30 ng/g). This result is unsurprising given that AO246 is not manufactured in Canada (Environment Canada, 2012) and the total quantity of AO246 imported into Canada in 2006 was 1–10 tonnes (Environment Canada, 2011). In addition, the primary end-use application of AO246 in Canada is as an antioxidant in hydrocarbon fuels such as jet fuel, gasoline, diesel, and biodiesel, which have limited applications in indoor environments (Environment Canada, 2012). Surprisingly, its isomer, DTBSBP, was detected in many more samples (66%) and at much higher concentrations (<MQL–885 ng/g, GM: 6.09 ng/g) than AO246, which might indicate that the products of its industrial applications are more likely to be found in indoor environments in Canada than are those of AO246. Indeed, 17 tonnes of DTBSBP was imported into Canada in 2006. It is mainly used as an antioxidant in plastics and polyurethane, which are largely used in indoor environments (Environment Canada, 2010). 2,4-Di-*tert*-amylphenol (D*t*AP, <MQL–172 ng/g, GM: 1.92 ng/g) and BHA (<MQL–86.6 ng/g, GM: 2.38 ng/g) were only detected in <25% of the samples. To the best of our knowledge, this is the first report of SPAs in indoor environments in Canada, and the first-ever report of 4*t*BP in environmental samples.

As shown in Fig. 2, among the eight SPAs detected in the indoor dust samples, BHT was the top contributor, contributing 0.1%–98.2% (mean: 56.9%) to ∑SPAs. This is in line with reported SPA composition profiles in various environmental matrices such as sewage sludge and river sediment that show that BHT is also the most important congener in those matrices (Liu et al., 2015a; Liu et al., 2015b). As the dominant congener, the concentrations of BHT (GM: 592 ng/g, $n = 83$) in dust present here are much lower than those in dust collected from China (GM: 2270 ng/g, median: 1880 ng/g, $n = 55$) and United States (median: 4310 ng/g, $n = 14$) (Liu et al., 2017; Wang et al., 2016). A similar trend was found in a recent study that the concentrations of BHT in sludge samples collected in Canada (median: 477 ng/g, $n = 21$) are much lower than those in sludge collected from China (GM: 4140 ng/g, median: 2350 ng/g, $n = 55$) and United States (median: 4170 ng/g, $n = 7$) (Liu et al., 2015b; Lu et al., 2019; Wang and Kannan, 2018), suggesting Canada might consume lower volume of BHT than Canada and United States do. DBP and 4*t*OP were the next most significant congeners, contributing 0.02%–89.8% (mean: 19.4%) and 0.1%–75.0% (mean: 15.4%) to ∑SPAs, respectively. The other five SPA targets, including 4-*t*BP, AO246, DTBSBP, BHA, and D*t*AP, contributed little (mean: <5.3%) to ∑SPAs.

Table 1
Descriptive statistics of the measured SPA and transformation product concentrations (ng/g) in the indoor dust samples ($n = 83$).

Compounds	GM[a]	Median	95th	Range	Quantification rate[b] (%)
Synthetic phenolic antioxidants (SPAs)					
BHT	658	821	4433	<MQL–15178	96
DBP	161	254	759	<MQL–2272	96
4-*t*BP	19.7	45.0	240	<MQL–1343	53
4-*t*OP	127	159	416	<MQL–844	93
DTBSBP	6.09	11.8	65.7	<MQL–885	66
AO246	0.30	<MQL	8.01	<MQL–177	11
D*t*AP	1.92	<MQL	94.4	<MQL–172	25
BHA	2.38	<MQL	<MQL	<MQL–86.6	4
∑SPAs	1490	1644	5114	67.2–15,464	100
BHT transformation products (TPs)					
BHT-OH	40.1	61.3	144	<MQL–280	87
BHT-CHO	32.9	46.5	159	<MQL–386	92
BHT-Q	325	370	1554	<MQL–4770	90
BHT-quinol	379	435	2295	<MQL–7673	100
∑TPs	883	974	4106	40.4–12,693	100

[a] GM: geometric mean.
[b] Quantification rate: calculated if any of the corresponding target analytes could be quantified.

3.2. TPs in indoor dust

Previous studies have demonstrated that BHT can be transformed both in vivo and in vitro via oxidation of the aromatic ring or alkyl substituents, leading to the generation of TPs such as 2,6-di-*tert*-butyl-4-hydroxy-4-methyl-2,5-cyclohexadienone (BHT-quinol), 2,6-di-*tert*-butyl-4-(hydroxymethyl)phenol (BHT-OH), BHT-CHO, and BHT-Q (Matsuo et al., 1984). In addition, oxidation of BHT has also been observed under visible light photo-irradiation (Criado et al., 2007). Some TPs of BHT have been receiving more attention than the parent chemical due to their reportedly stronger toxicity effects (Nagai et al., 1993).

As shown in Table 1, all four TPs were detected in most of the indoor dust samples (>87%), with ∑TPs in the range of 40.4–1.27e4 ng/g (GM: 883 ng/g). These concentrations are even higher than those of the parent molecule, BHT (GM: 658 ng/g). Among the four TPs, BHT-quinol and BHT-Q were detected at relatively high concentrations, ranging from <MQL–7.67e3 ng/g (GM: 379 ng/g) and <MQL–4.77e3 ng/g (GM: 325 ng/g), respectively. As shown in Fig. 2, BHT-quinol and BHT-Q were the top contributors to ∑TPs, accounting for 12.3%–90.1% (mean: 45.7%) and 1.5%–80.2% (mean: 42.3%) of ∑TPs, respectively. BHT-OH and BHT-CHO were observed at relatively low concentrations of <MQL–280 ng/g (GM: 40.1 ng/g) and <MQL–386 ng/g (GM: 32.9 ng/g) and contributing only 6.5% and 5.5% to ∑TPs, respectively. The composition profiles of TPs were generally in line with previous reports from indoor environments in China that found that BHT-quinol and BHT-Q were the major contributors to ∑TPs (Liu et al., 2017). These results may indicate that similar transformation pathways of BHT occur in different indoor environments. However, the composition profiles of TPs in the indoor dust are different from those reported for human serum samples from United States donors, where BHT-CHO and BHT-Q were the primary congeners (Liu and Mabury, 2018a). The differences in the composition profiles between the indoor dust and human serum samples might suggest that the transformation pathways of BHT in indoor environments are different from those in humans.

3.3. Correlation analysis

In order to investigate the abundance difference of SPAs and TPs in different indoor environments, the 83 indoor dust samples were divided into two groups: office indoor dust samples ($n = 54$), and home indoor dust samples ($n = 29$). No significant differences ($p > 0.05$) were found for either ∑SPAs and ∑TPs between the office (GM of 1.24e3 and 751 ng/g, respectively) and home indoor dust samples (GM of 2.09e3 and 1.20e3 ng/g, respectively), implying that SPAs and related TPs are ubiquitously present in various indoor environments. This result is reasonable, considering that both home and office indoor environments use many products that tend to contain high concentrations of SPAs, such as foams and plastics (Lanigan and Yamarik, 2002). Furthermore, the office and home indoor dust samples had similar composition profiles in that BHT was the major congener contributing to ∑SPAs (Fig. 2). This is generally in accordance with the production volumes of SPAs in North America: BHT is the most-often used SPA, with

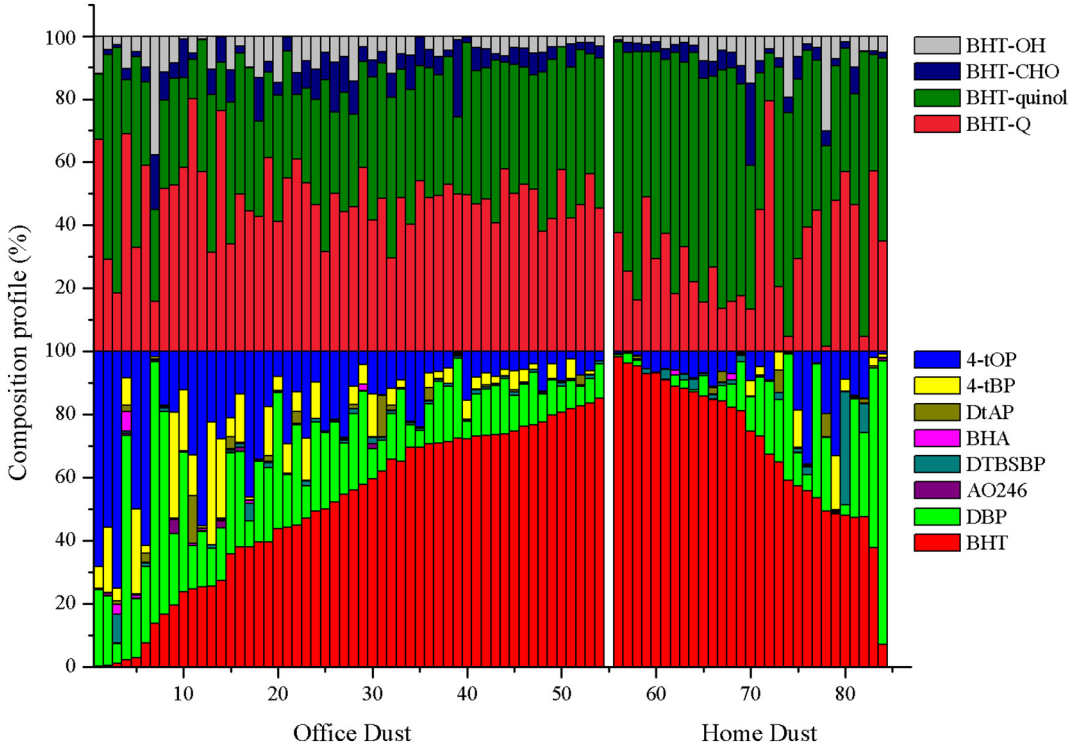

Fig. 2. Composition profiles of the SPAs and TPs in the office and home dust samples. The x-axis represents sample number.

production volumes exceeding 7000 tones/year in North America (OECD, 2002). Although the production volumes of DBP (9200 tonnes/year) and 4-*t*OP (22680–45,360 tonnes/year) are similar with or higher than that of BHT, they are primarily used as intermediates to produce other antioxidants and p-*tert*-octylphenol-based resins, respectively, instead of being used as antioxidants (Danish Ministry of Environment, 2013; USEPA, 2015), which can explain their relatively low detected concentrations. Finally, the office and home indoor dust samples shared similar TP composition profiles in that BHT-quinol and BHT-Q were the primary TPs, which indicates that similar transformation pathways of BHT are relevant in various indoor environments.

Multivariate analysis of the analyte concentrations in the indoor dust samples showed significant positive correlations among the most frequently detected SPAs (BHT and DBP; $R = 0.297$, $p < 0.01$, Table 2), indicating that these SPAs likely have common release pathways and/or similar behaviors in indoor environments. However, no strong relationship was found between 4-*t*OP and most of the other SPAs (BHT, DBP, DTBSBP, and 4-*t*BP; $p > 0.05$), which might imply that 4-*t*OP has a different source from the other SPAs typically found in indoor environments. As reported, 4-*t*OP is mainly used to manufacture p-*tert*-octylphenol-based resins other than use as an antioxidant (Danish Ministry of Environment, 2013), which suggests its different source in indoor environments than the other SPAs. Strong positive relationships were found among the four TPs ($R = 0.567$–0.780, $p < 0.05$). Furthermore, all the TPs were strongly related to their parent chemical BHT in the indoor dust ($R = 0.711$–0.910, $p < 0.01$), which may indicate that the TPs have a common source and similar environmental behaviors in indoor environments.

3.4. Human exposure to SPAs and TPs via office and home dust ingestion

The estimated daily intake (EDI) via indoor dust ingestion was calculated according to the equation shown below:

$$EDI = C \times DIR \times IEF/BW \quad (1)$$

where C is the concentration of the SPAs and TPs in the dust samples, DIR is the dust ingestion rate (g/day), IEF is the indoor exposure fraction, and BW is body weight (kg). The body weights used for toddlers and adults were 13 and 80 kg, respectively, and DIRs of 0.1 and 0.05 g/d were used for toddlers and adults, respectively (Zheng et al., 2017). According to a previous study, the IEFs are 63.8% and 22.3% for home and office, respectively, for adults (Abdallah and Covaci, 2014). For toddlers, the IEFs are 100% and 0% for home and office, respectively (Abdallah and

Table 2
Spearman's analysis of the target concentrations in indoor dust.

	BHT	DBP	DTBSBP	4-*t*BP	4-*t*OP	BHT-OH	BHT-quinol	BHT-CHO	BHT-Q
BHT	1								
DBP	0.297**	1							
DTBSBP	0.612**	0.088	1						
4-*t*BP	0.061	0.460**	0.173	1					
4-*t*OP	0.140	0.094	0.157	0.211	1				
BHT-OH	0.711**	0.405**	0.508**	0.149	0.257*	1			
BHT-quinol	0.910**	0.158	0.655**	0.023	0.241*	0.768**	1		
BHT-CHO	0.738**	0.264*	0.493**	0.143	0.326**	0.780**	0.775**	1	
BHT-Q	0.770**	0.273*	0.505**	0.232*	0.219*	0.567*	0.769**	0.653**	1

** Significant at the $p < 0.01$ level (two-tailed)
* Significant at the $p < 0.05$ level (two-tailed).

Covaci, 2014). The GM concentrations were used to calculate the GM EDIs for both toddlers and adults, and the worst-case EDIs were calculated based on the 95th percentile concentrations. As shown in Table 3, the GM and 95th percentile EDIs of ∑SPAs for adults via ingestion of a combination of the office and home indoor dust were 1.01 and 3.22 ng/kg BW/day, respectively. The GM and 95th percentile EDIs of ∑TPs for adults were 1.65 and 5.62 ng/kg BW/day, respectively. The toddler EDIs, which are based solely on ingestion of home dust, were much higher for both ∑SPAs (GM: 16.1 ng/kg BW/day, 95th percentile: 50.6 ng/kg BW/day) and ∑TPs (GM: 9.20 ng/kg BW/day, 95th: 38.8 ng/kg BW/day), due to their lower body weight and high dust ingestion rate. BHT, which was found to be the major SPA congener in this study, was previously determined to have an EDI via food intake of 130 μg/kg BW/day for people in Canada (Kirkpatrick and Lauer, 1986). That the food intake EDIs determined by previous studies are so much higher than the dust ingestion EDIs determined in the present study suggests that dust ingestion is not a major human exposure pathway for BHT.

The potential health risk arising from SPAs from indoor dust ingestion was assessed as a hazard quotient (HQ), which was calculated as the ratio of exposure dose (i.e., EDI) to the acceptable daily intake (ADI). BHT is the only congener with a recommended ADI. The ADI of BHT for humans was set as 0.25 mg/kg BW/day by European Food Safety Authority (Lanigan and Yamarik, 2002). The HQs of BHT based on the calculated EDI were far below 1 for both adults (GM: $2.32e^{-6}$, 95th percentile: $1.20e^{-5}$) and toddlers (GM: $4.00e^{-5}$, 95th percentile: $1.93e^{-4}$), which indicates that human exposure to BHT through indoor dust ingestion is not likely to cause immediate health risks to the Canadian population. It should be noted that ADIs of other SPAs and their TPs are not currently available. The health risk of exposure to several SPAs and TPs simultaneously via indoor dust ingestion should be further evaluated, as synergistic effects were observed in the induction of apoptosis when human promyelocytic leukemia cell lines and human squamous cell carcinoma cell lines were simultaneously exposed to BHT and BHA (Saito et al., 2003).

4. Conclusions

Eight SPAs (67.2–1.55e4 ng/g, GM: 1.49e3 ng/g) were identified in indoor dust samples collected from different offices and homes located in Toronto, Canada. No significant concentration difference was found for either ∑SPAs or ∑TPs between the office and home indoor dust samples ($p > 0.05$), suggesting the prevalence of these emerging chemical contaminants in various indoor environments. BHT was the major congener in both home and office indoor dust samples. Four TPs of BHT (40.4–1.27e4 ng/g, GM: 883 ng/g) were also detected in the indoor dust samples with concentrations similar to their parent chemical (GM of BHT: 642 ng/g). To the best of our knowledge, this is the first report of the occurrence of these chemical contaminants and related TPs in indoor environments in Canada. Furthermore, this is the first report of 4-*t*BP in any environmental sample. The present investigation shows that people are ubiquitously exposed to SPAs via indoor dust in Canada; however, human exposure to BHT via ingestion of indoor dust ingestion is a minor exposure pathway compared to that via food intake. However, only limited numbers of indoor dust samples ($n = 83$) collected in one city (Toronto) were investigated in this study. Further studies are warranted to include more samples from different locations and investigate whether other SPA congeners and TPs also exist in Canadian environment.

Table 3
Estimated daily intakes (EDI, ng/kg BW/day) of SPAs and TPs by ingestion of indoor dust for toddlers and adults in Canada.

Compounds	Toddlers		Adults	
	GM	95th percentile	GM	95th percentile
Synthetic phenolic antioxidants (SPAs)				
BHT	10.0	48.2	0.58	2.99
DBP	0.88	6.92	0.07	0.45
4-*t*BP	0.05	1.46	0.01	0.12
4-*t*OP	0.63	2.60	0.06	0.22
DTBSBP	0.06	1.15	0.004	0.07
∑SPAs	16.1	50.6	1.01	3.22
BHT transformation products (TPs)				
BHT-OH	0.43	1.70	0.03	0.10
BHT-CHO	0.30	1.87	0.02	0.12
BHT-Q	2.21	10.6	0.16	0.78
BHT-quinol	5.09	29.7	0.30	1.76
∑TPs	9.20	38.8	0.58	2.56
Sum	26.4	85.9	1.65	5.62

AO246, DtAP, and BHA were not listed due to low concentrations and low detection frequency.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.03.495.

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